poured upon ice gave a dark green, gelatinous precipitate which dried out in the oven to a hard, black solid; yield, 0.8 g. The color of an aqueous solution of the sodium salt was deep blue, which changed to dark green when acidified. Hypochlorite oxidation of this supposititious sodium sulfonate failed to yield any dye.

Summary

1. By the action of *o*- and *m*-nitrobenzoyl chlorides upon the zinc salt of 2-amino-5-methylphenyl mercaptan, the corresponding 2-nitrophenylbenzothiazoles have been prepared.
2. Reduction of these nitro derivatives gave amines isomeric with dehydrothio-*p*-toluidine.
3. From the *m*-aminophenyl derivative, by hypochlorite oxidation of its sodium sulfonate, a direct cotton dye was prepared, presumably isomeric with Chloramine Yellow (Colour Index No. 814), but giving paler yellow shades. From the isomeric *o*-aminophenyl derivative, no similar dye could be obtained.

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[Contribution from the Physical and Chemical Laboratories of the Ohio State University]

ULTRAVIOLET ABSORPTION SPECTRA OF CYCLOHEXENE, ETHYL ETHER, METHYL-NORMAL-AMYL ETHER AND ETHYLENE CHLOROHYDRIN. A CORRECTION TO OUR PREVIOUS ARTICLE[1] UNDER THIS TITLE AND REPLY TO DR. DE LASZLO[2]

By Alpheus W. Smith, Cecil E. Boord, Clyde S. Adams and Charles S. Pease

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The results contained in our previous paper have been challenged by Dr. de Laszlo with the contention that the absorption was in every case due to benzene. It is concluded "that benzene may have been present as an impurity either in the material or apparatus in amounts sufficient to explain the results as reported by these authors."

After a careful re-examination of ethylene chlorohydrin, methyl-*n*-amyl ether and ethyl ether in the light of these contentions we are compelled to admit that the results shown in our paper are due to benzene. It will be of general interest to know wherein this error arose.

As to cleanliness let it be said that it has been our unvarying practice to wash the absorption cells with chromic acid mixture after each run and that blank exposures through these same cells showed no absorption. One comes then to the second alternative, namely, that the compounds examined contained benzene as a common impurity. A careful re-exami-

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[1] Smith, Boord, Adams and Pease, This Journal, 49, 1335 (1927).

[2] De Laszlo, *ibid.*, 49, 2106 (1927).

nation of the compounds has shown that this was in fact the case and that they contained the impurity when we received them. This is confirmed by the results obtained by Orndorff, Gibbs, McNulty and Shapiro and contained in a paper which has been submitted to THIS JOURNAL. When these substances are repurified with a fore-knowledge of the fact that they contain benzene, the impurity can be partially or wholly removed, with the result that the absorption pattern is either greatly diminished in intensity or entirely absent.

It seems desirable to know how benzene was introduced into these compounds. Letters from the leading manufacturers in answer to inquiries as to the possibility of diethyl ether containing a trace of benzene are about equally divided between those who cannot account for its presence and those who state frankly that ether is sometimes prepared from alcohol which has been denatured by benzene. To quote from the letter of one producer:

> The Internal Revenue Bureau have authorized two special denatured alcohols for use in the manufacture of ether.
>
> 1.—S. D. Formula 2-B is made up as follows: "To 100 gallons of ethyl alcohol add $^1/_2$ gallon of benzol."
>
> 2.—S.D. 13-A is made up as follows: "To 100 gallons of ethyl alcohol add 10 gallons of sulfuric ether."
>
> "We hold permits to use either of these formulas."

Over a period of about three years we continuously found the absorption bands not only in the U.S.P. ether but also in the C.P. anhydrous ether (distilled over sodium). During this period two different brands of diethyl ether were used with perfectly uniform results. Several brands now on the market do not show the impurity, including one of those in which the absorption was previously found. Some producers state they have not used alcohol denatured according to Formula 2–B during the past year. Since the methyl-*n*-amyl ether is prepared by use of the Grignard reaction, the trace of benzene in that substance can now be attributed to the anhydrous ether used in its preparation.

In the light of these facts we wish to raise two questions of general interest. The first is: How generally does benzene occur as an impurity in liquid organic compounds of highest quality? It would seem that since benzene is frequently used in the dehydration processes and also in the dehydration of many crude products, its presence must be suspected in all compounds prepared in this way. It now appears that it may also be introduced whenever commercial U.S.P. ether or C.P. anhydrous ether (distilled over sodium) is used in a preparation process. These two groups serve to bring a very large number of liquid organic compounds under the suspicion of containing benzene. Certainly the amount of impurity is no more than a trace, but the possibility of its presence should be generally recognized.

The second question is: Does anesthetic ether ever contain benzene? We have examined four brands of anesthetic ether. In only one case was an absorption pattern obtained and this was much fainter than has been found with U.S.P. ether or C.P. anhydrous ether containing the impurity.

The latter part of Dr. de Laszlo's article does not deal with a question of fact but rather with the interpretation of ultraviolet absorption spectra. Since the validity of the experimental results contained in our paper has been disproved, a further discussion of interpretation does not seem profitable at this time. However, on the basis of the quantum theory, we find little reason for supposing any absorption or emission spectrum to be essentially continuous.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF HYNSON, WESTCOTT & DUNNING]

SALICYLSULFONPHTHALEIN AND ITS TETRABROMO AND MONOMERCURY DERIVATIVES

BY WILTON C. HARDEN

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Since the synthesis of the first sulfonphthaleins by Remsen and his students[1] many new members of this class of compounds have been described by Orndorff and his co-workers,[2] Clark and Lubs,[3] Cohen[4] and others.

The purpose of the present paper is to describe still another sulfonphthalein, namely, salicylsulfonphthalein. The only mention of this compound in the literature is contained in some German patents[5] describing certain dyestuffs prepared by the condensation of *o*-sulfobenzaldehyde with various phenols, cresols and substituted phenols and cresols. In this manner salicylic acid was condensed with *o*-sulfobenzaldehyde to give a red dye.

The author has prepared this compound by condensing salicylic acid with the anhydride of *o*-sulfobenzoic acid and found it to possess some interesting properties. Its tetrabromo and its monohydroxymercuri derivative have also been prepared and will be discussed.

Since nearly all of the sulfonphthaleins are useful indicators in the determination of hydrogen-ion concentration and since salicylsulfon-

[1] (a) Remsen, *Am. Chem. J.*, **6**, 180 (1884); (b) Remsen and Saunders, *ibid.*, **17**, 352 (1895); (c) Sohon, *ibid.*, **20**, 257 (1898).

[2] (a) Orndorff and Sherwood, THIS JOURNAL, **45**, 486 (1923); (b) Orndorff and Shapiro, *ibid.*, **46**, 2856 (1924); (c) Orndorff and Purdy, *ibid.*, **28**, 2212 (1926); and others.

[3] Clark and Lubs, *J. Wash. Acad. Sci.*, **5**, 609 (1915); **6**, 481 (1916); **6**, 483 (1916).

[4] (a) Cohen, *U. S. Public Health Reports*, **38**, 199 (1923); (b) **41**, 53, 3051 (1926).

[5] Friedländer, (1908–1910), vol. 9, p. 195; D. R. P. 189,938–198,909 and others.